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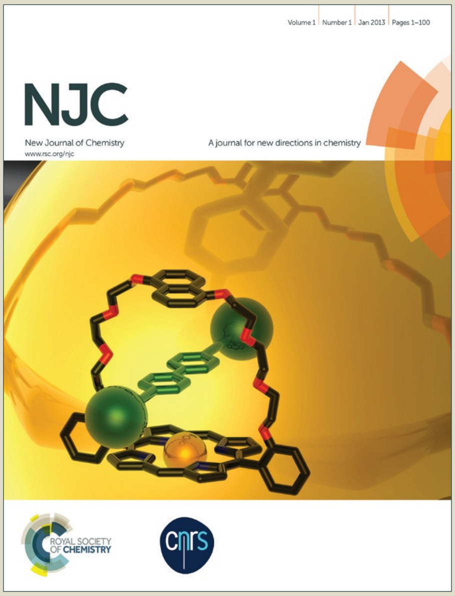

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ARTICLE

Effective Hydrodeoxygenation of Dibenzofuran by Bimetallic Catalyst in Water

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Effective hydrodeoxygenation (HDO) of dibenzofuran (DBF) catalyzed by bimetallic Ni/Pt catalyst in water was demonstrated at 200 °C and 1.2 MPa H_2 pressure. The bimetallic catalysts prepared by a wet chemical method exhibit prominent activity that overcomes the limitations of single metal catalyst Ni or Pt. The yield of hydrodeoxygenation products can be achieved up to 90%. Reaction results indicate that the conversion of dibenzofuran was affected by the reaction temperature and H_2 pressure. The deoxygenation selectivity was strongly depended on reaction temperature. The reaction pathway was also proposed.

1. Introduction

Coal tar, as an important by-product of coal processing industry, contains a wide-range of compounds with different molecular weights and functionalities [1, 2]. They can cause ubiquitous and persistent environmental pollutants to be released to the environment [3, 6]. Dibenzofuran (DBF) is one of the typical oxygen-containing compound in coal tar. Hydrodeoxygenation (HDO) of DBF can convert O-containing wastes to usable products [7]. In addition, DBF is an important intermediate in the biomass gasification [8]. High oxygen content of bio-oils leads to their high viscosity, low heating value and poor thermal stability [9, 10]. As we known, catalytic HDO is a promising process to upgrade the bio-oils to hydrocarbon fuels. Therein, DBF was chosen as the HDO model compound for our research.

Conventional CoMo sulfide and NiMo sulfide supported catalysts used for HDO of DBF have been conducted, and several HDO reaction pathways of DBF have been proposed [11, 12]. However, there are several disadvantages of metal sulfide catalysts, such as extra sulfide is needed to maintain the activity of the catalyst [13], and sulfur may be introduced into the products at the process and result in products contamination. Besides sulphide /oxide catalysts, noble metal (Ru, Rh, Pd, Pt, etc.) catalysts are known to be efficient for HDO of oxygen-containing aromatics under mild conditions [14-17]. Recently, Pt supported on mesoporous ZSM-5 zeolites was used as catalyst for HDO of DBF at 200°C, 4MPa H_2 pressure [18]. And HDO of DBF over supported Pt, Pd, and Ru catalysts at 280-300 °C and 3MPa H_2 were reported by C. Liang et al. [19-21]. These catalytic performances of HDO reactions were attributed to hydrogenation ability of the active metal sites and cleavage of the C–O bond promoted by acidic sites, which requires a nearly completely saturated benzene ring before the removal of heteroatom oxygen. Besides precious metal catalysts, supported Ni catalysts in the absence of adjacent acid sites can also hydrogenolyze aromatic ether bonds on Ni sites, which was disclosed by A. Lercher group [22-24]. Noble metal (Pt, Ru, Pd) have superior hydrogenation activity [25-26] and Ni catalysts have high selectivity and moderate activity for HDO of oxygen-containing aromatics [27-30]. Therefore, the combination of these two kinds of metals to be bimetallic catalysts for HDO of DBF was taken into consideration in this study.

Many kinds of bimetallic catalysts have been reported for different reaction purpose, such as [31-33], Ni/Cu [34] and Fe/Pd, Ni/Pd, Ni/Au bimetallic catalysts [35-40]. The method with the addition of noble metal to Ni-based catalyst to improve the catalytic activity of aromatic C-O cleavage in aqueous phase was developed by J. Zhang et al [39, 40]. Ni/M (M = Ru, Rh, and Pd) catalysts inherited the advantages of both components, in which noble metal increased the hydrogenation activity of catalyst, and Ni modified the selectivity of noble metal to favor the C–O bond cleavage. The synergistic effects of the bimetallic catalyst lead to the improved

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catalytic performance. In addition, as catalytic HDO of oxygen-containing aromatics will produce water as byproduct, water-tolerant catalysts would be more beneficial choices for this type of reaction. This approach also makes the separation of HDO products easier from the reaction mixture.

2. Experimental

2.1. General

All reagents were purchased from commercial sources and used without treatment. Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai12 microscope operating at 120 kv. X-ray photoelectron spectroscopy (XPS) were performed on a ESCALAB 250Xi spectrometer, using a Al Kα X-ray source (1350 eV of photons) and calibrated by setting the C 1s peak to 284.80 eV. Catalytic hydrodeoxygenation reactions were conducted in an EYELA ChemiStation PPV-CTRL1 high pressure parallel reactor. Hydrodeoxygenation products were analyzed by gas chromatography (GC) on an Agilent 7890A gas chromatograph with a flame ionization detector (FID), equipped with HP-5 capillary columns, and gas chromatography/mass spectroscopy (GC/MS) with an thermo scientific trace1300 GC/MS instrument equipped with TR-5MS columns. Most products were known compounds and identified by comparison of their physical and spectra data with those of authentic samples.

2.2. Preparations of Ni_xM_{100-x} Catalysts

2.2.1. Preparations of Ni_xPt_{100-x} Catalysts

A series of Ni_xM_{100-x} (x/molar percentage of Ni = 0, 75, 80, 85, 86, 90, 100) catalysts were prepared using a wet chemical method by aqueous phase reduction of metal salts with $NaBH_4$, employing PVP as a stabilizing agent [39-41]. A water solution (4 mL) of metal salt or metal salts mixture and PVP were added to a 20 mL specially reinforced tube. To this mixture, a freshly prepared aqueous solution of $NaBH_4$ was added in one portion under vigorous stirring. A black colloid was obtained immediately. A typical preparation procedure for $Ni_{86}Pt_{14}$ is described here. A water solution (4 mL) of $NiCl_2·6H_2O$ (14 mg, 0.0589 mmol), $PtCl_6·6H_2O$ (5 mg, 0.0096 mmol), and PVP (100 mg, 0.90 mmol based on monomer) were added to a 20 mL specially reinforced tube. To this mixture, a freshly prepared aqueous solution of $NaBH_4$ (13.5 mg, 0.35 mmol, in 2 mL H_2O) was added in one portion under vigorous stirring. A black colloid was obtained immediately.

2.2.2. Preparations of Ni_xPd_{100-x} Catalysts

Ni_xPd_{100-x} (x/molar percentage of Ni = 0, 75, 80, 85, 86, 90, 100) catalysts were prepared using a wet chemical method by aqueous phase reduction of metal salts with $NaBH_4$, employing PVP as a stabilizing agent. Because $PdCl_2$ is not dissolved in water, so $PdCl_2$ was dissolved in an aqueous solution containing NaCl to form Na_2PdCl_4. A typical preparation procedure for $Ni_{85}Pt_{15}$ is described here. $PdCl_2$ (1.8mg, 0.0103 mmol) was dissolved in an aqueous solution (4 mL) containing NaCl (3.5mg, 0.0618 mmol) to form Na_2PdCl_4. To this solution, $NiCl_2·6H_2O$ (13.8mg, 0.0582 mmol), and PVP (100 mg, 0.9 mmol based on monomer) were added, and the suspension was stirred for 30 s for dissolution. To this mixture, a freshly prepared aqueous solution of $NaBH_4$ (13.5 mg, 0.35 mmol, in 2 mL H_2O) was added in one portion under vigorous stirring. A black colloid was obtained immediately.

2.3. Characterizations of Ni_xM_{100-x} Catalysts

2.3.1. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai12 microscope operating at 120 kv. The freshly prepared catalyst solution was passivized by bubbling with N_2 for 20 minutes, to prevent the oxidation of the catalysts, immediately after synthesis. TEM samples were prepared by diluting the solution (0.05 mL) with methanol (3 mL), following which one drop of the solution was placed on a carbon film covered copper grid and dried under air.

2.3.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were performed on a ESCALAB 250Xi spectrometer, using a Al Kα X-ray source (1350 eV of photons) and calibrated by setting the C 1s peak to 284.80 eV. The fresh catalyst solution (10mL) was mixed with acetone (80 ml). The mixture was centrifuged and semi-solid material at the bottom of the centrifugation was collected, dried under vacuum, and analyzed by XPS. Note that Ni atoms in the oxide form due to post-oxidation during sample preparation.

2.4. Hydrodeoxygenation Reaction with Dibenzofuran

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In a typical HDO experiment, a freshly prepared catalyst (0.0685 mmol) colloid was transferred into the reactor (20 mL) with a magnetic stirrer for the hydrodeoxygenation. The substrate DBF (38 mg, 0.228 mmol) was added. After flushing with H_2 four times, the reactor was charged with 1.2 MPa of H_2 and the temperature was raised to 200 °C with a stirring speed of 500 rpm. After the reaction complete, the mixture was cooled to ambient temperature, extracted with ethyl acetate (20 mL) and the organic phase was analyzed by GC/MS.

3. Results and discussion

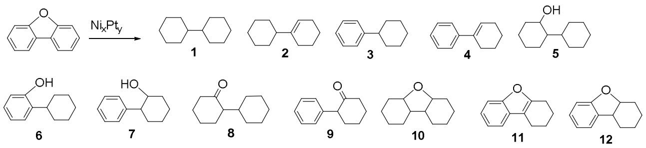

Fig.1. Twelve products identified after of Dibenzofuran hydrodeoxygenation

Table 1. Hydrodeoxygenation of dibenzofuran over Ni, Pt and Ni_xPt_{100-x} catalysts.

Entry	**Catalyst**	**Selectivity [a] (%)**			**Conv. (%)**	**Standard Error [e]**
		A [b]	**B [c]**	**C [d]**		
1	Ni	73	15	12	59	3.8
2	Pd	2	0	98	99	0.5
3	Pt	32	27	41	99	0.5
4	$Ni_{75}Pd_{25}$	2	2	96	64	3.7
5	$Ni_{85}Pd_{15}$	3	2	95	78	3.5
6	$Ni_{75}Pt_{25}$	63	11	26	63	2.8
7	$Ni_{80}Pt_{20}$	70	13	17	75	2.6
8	$Ni_{82}Pt_{18}$	77	10	13	82	2.4
9	$Ni_{86}Pt_{14}$	92	5	3	99	0.8
10	$Ni_{88}Pt_{12}$	82	12	6	92	2.0
11	$Ni_{90}Pt_{10}$	75	13	12	81	2.4

[a] Reaction conditions: 0.228 mmol Dibenzofuran, 6 mL freshly prepared aqueous solution containing 0.44 mmol PVP, 0.0685mmol catalyst, H_2, 1.2MPa, 200 °C, 10h.

[b] Hydrodeoxygenation products (compounds **1**- **4**).

[c] Hydrogenolysis products (compounds **5**- **9**).

[d] Hydrogenation products (compounds **10**- **12**).

[e] Standard errors obtained from3 groups of parallel experiments.

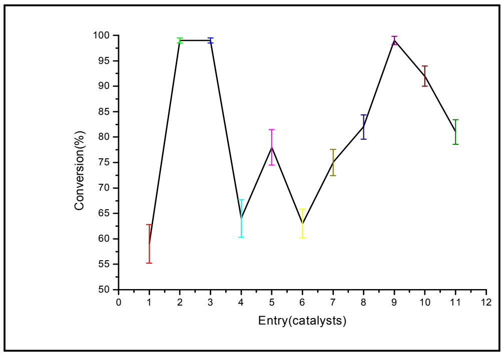

Figure2. The plot of the reaction conversions

3.1. Products Distribution of Dibenzofuran Hydrodeoxygenation

At first, monometallic catalysts (Ni, Pd and Pt) were used for the HDO of dibenzofuran (Table 1). Twelve main products were identified by GC-MS analysis (**1-12**; see Fig. 1) and there were no single-ring products observed from the HDO of DBF. Compounds **1-4** which lost the oxygen were derived from the hydrogenation deoxygenation of the substrate. Compounds **5-9** were products retaining one of C-O bond through another C-O bond hydrogenolysis. Compounds **10-12** were products generated by hydrogenation of the substrate without the cleavage of the C-O bond. So, the products were categorized as hydrodeoxygenation products **A**: **1–4**, hydrogenolysis products **B**: **5–9** and hydrogenation products **C**: **10-12**. Ni monometallic catalyst achieved 59% conversion and 73% selectivity toward hydrodeoxygenation product (entry 1). Pt monometallic catalyst showed higher activity (entry 3) with 99% conversion of DBF, but the hydrodeoxygenation product selectivity was only 32%. Pd monometallic catalyst has poorer hydrodeoxygenation selectivity with 99% conversion and 2% hydrodeoxygenation product selectivity. Ni catalyst showed a highest selectivity towards hydrodeoxygenation products although the reaction did not have the highest conversion. Then, we evaluated the performance of several bimetallic catalysts to

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improve the activity of the Ni catalysts and the product selectivity over different catalysts were summarized in table 1. The plot of the reaction conversions as a function of the catalysts used were showed in Figure 2. The Error bars on data points of figure2 were the results of 3 measurements. By incorporating Pd into Ni, the Ni/Pd catalysts did not improve the reaction selectivity as desired. The main products were also the hydrogenation products, which further indicated that Pd catalyst has higher hydrogenation activity than deoxygenation activity. By incorporating Pt into Ni, as Ni has a low content the products selectivity were similar with pt monometallic catalyst. With the increasing of Ni content, the Ni/Pt catalysts inherited the advantages of both components and $Ni_{86}Pt_{14}$ catalyst has the best performence with 99% conversion and 92% hydrodeoxygenation product selectivity. The selectivity of higher-Ni-content catalysts was maintained while the activity dropped gradually. Thus, $Ni_{86}Pt_{14}$ was chosen for further investigation. The reaction conditions were optimized and the results were summarized in Table 2, Table3 and Table4

3.2. Effect of Reaction Conditions

At 200 ^{o}C, the hydrodeoxygenation products selectivity was up to 92% with the excellent high selectivity of compound **3** with 88% selectivity. At 150 ^{o}C, the hydrodeoxygenation products selectivity was 10%, and the yield of **3** decreased to 9 %. In contrast, **6** and **7** increased to 63 % which were not detected at the reaction condition of 200 ^{o}C. At lower temperature (100 ^{o}C), the reaction became slow, thus, the hydrodeoxygenation selectivity only turned to 22 % and the total conversion was 9 % (Table 2). Above all, it could be concluded that temperature has great influence on total conversion and catalyst hydrodeoxygenation selectivity, which may due to the strong aromatic ether linkage of dibenzofuran.

Reaction pressure was another important influencing factor for the hydrodeoxygenation reaction. The conversion of DBF increases sharply from 59% to 100% when hydrogen pressure changes from 0.8 to 1.4 MPa. High hydrogen pressure may largely promotes the hydrogenation of aromatic rings of DBF to yield more product **11** and **12**, and then C–O bond cleavage is enhanced with up to 92% selectivity toward hydrodeoxygenation products and product **3** was the main product with 88% yield (Table 3, entry 4). The reaction time also affected the conversion rate of the substrate and the selectivity of the products. When reacting for 10 h the total conversion can reach above 99% and the selectivity of product **3** reached 88% (Table 4).

3.3. Transmission electron microscopy (TEM)

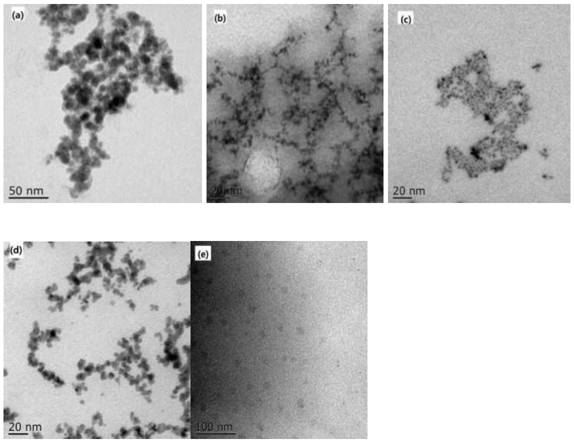

Figure3. (a) TEM image of Ni. (b) TEM image of $Ni_{86}Pt_{14}$. (c) TEM image of Pt. (d) TEM image of Pd. (b) TEM image of $Ni_{85}Pd_{15}$.

Transmission electron microscopy (TEM) was applied to probe the structure of the bimetallic catalyst, which indicates that the $Ni_{86}Pt_{14}$ catalyst is spherical with a diameter of 5.0 ± 0.5 nm (see Figure 3 b), similar to pure Pt particle (3.0 ± 0.5 nm) (see Figure 3 c) but smaller than the Ni catalyst (11.5 ± 3.5 nm) (see Figure3 a). $Ni_{85}Pd_{15}$ catalyst is spherical with a diameter of 10 nm ± 1.5 nm (see Figure 3 e), similar to pure Ni particle but bigger than the Pd catalyst (5.0 ± 0.5 nm) (see Figure3 d). The structural features of the $Ni_{86}Pt_{14}$ catalyst corresponded to synergistic effect, which was well documented that the combination of two metals could result in drastically enhanced catalytic performance. Compared with $Ni_{86}Pt_{14}$ catalyst, $Ni_{85}Pd_{15}$ has a bigger diameter. The different structural features of $Ni_{86}Pt_{14}$ and $Ni_{85}Pd_{15}$ catalysts corresponded to the different reactivity and selectivity of these two bimetallic catalysts (see Table 1).

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Table 2. HDO of dibenzofuran over $Ni_{86}Pt_{14}$ catalyst under different reaction temperature.

Entry	**Temp. (°C)**	**Selectivity [a] (%)**												**Conv. (%)**
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	
1	100	0	0	14	8	0	0	0	0	0	0	42	36	9
2	150	0	0	9	1	2	2	61	2	0	0	3	20	79
3	200	2	0	88	2	0	0	0	5	0	0	3	0	99

[a] Reaction conditions: 0.228 mmol Dibenzofuran, 6 mL freshly prepared aqueous solution containing 0.0685 mmol $Ni_{86}Pt_{14}$ and 0.44 mmol PVP, 1200 KPa H_2, 10 h.

Table 3. HDO of dibenzofuran over $Ni_{86}Pt_{14}$ catalyst with different hydrogen pressure.

Entry	**P_{H2} (KPa)**	**Selectivity [a] (%)**												**Conv. (%)**
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	
1	800	2	12	61	8	0	0	0	3	1	0	8	5	59
2	1000	4	12	61	2	0	0	0	4	1	0	7	9	63
3	1200	2	0	88	2	0	0	0	5	0	0	3	0	99
4	1400	13	31	56	0	0	0	0	0	0	0	0	0	100

[a] Reaction conditions: 0.228 mmol Dibenzofuran, 6 mL freshly prepared aqueous solution containing 0.0685 mmol $Ni_{86}Pt_{14}$ and 0.44 mmol PVP, H_2, 200 °C, 10 h.

Table 4. HDO of dibenzofuran over $Ni_{86}Pt_{14}$ catalyst with different reaction time.

Entry	**Time (h)**	**Selectivity [a] (%)**												**Conv. (%)**
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	
1	1	0	0	46	6	0	0	0	6	3	0	10	29	26
2	5	2	4	42	29	1	0	0	9	1	0	6	6	85
3	10	2	0	88	2	0	0	0	5	0	0	3	0	99
4	15	2	1	82	1	0	0	0	6	0	0	4	4	100

[a] Reaction conditions: 0.228 mmol Dibenzofuran, 6 mL freshly prepared aqueous solution containing 0.0685 mmol $Ni_{86}Pt_{14}$ and 0.44 mmol PVP, 200 °C, 1200 KPa H_2.

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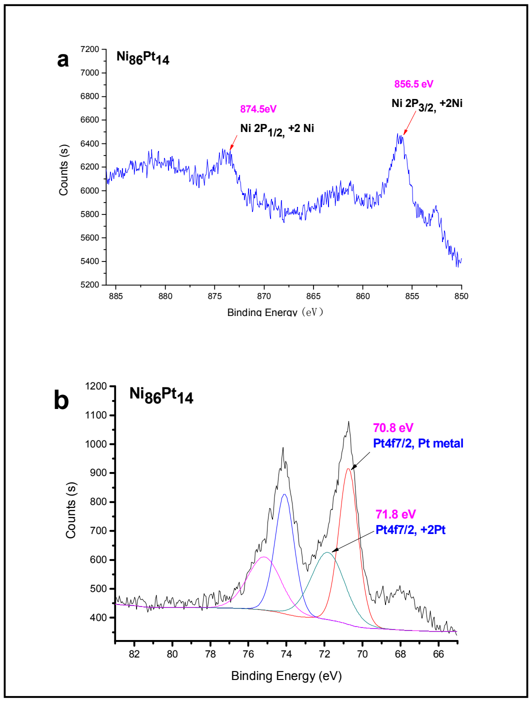


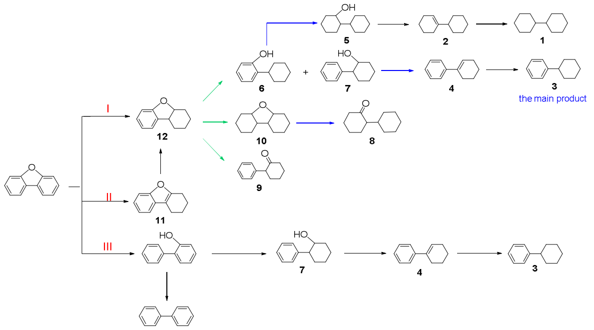
Figure 4. XPS spectra for Ni86Pt14 catalysts.

3.4 X-ray photoelectron spectroscopy (XPS)

XPS was employed to characterize valence state and surface composition of $Ni_{86}Pt_{14}$ catalysts. As shown in Figure 4, the spectra for $Ni_{86}Pt_{14}$ in Ni 2p region are revealing oxidation of Ni has occurred during the sample preparation. The appearance of the Pt 4f peak indicates the existence of near-surface Pt in the Ni84Pt16 catalyst. Using the Ni 2p3/2 and Pt 4f7/2 peak areas, the surface ratio of Ni/Pt can be determined as 8.4:1, which is higher than the precursors' ratio, 6.1:1, indicating that Ni is probably surface enriched.

3.5. Reaction Pathway of HDO of DBF over Ni/Pt Catalyst

According to the obtained experimental results, a proposed reaction pathway for dibenzofuran conversion over Ni/Pt catalyst under the current conditions is illustrated in Scheme 1. Typically, it is easy to achieve the hydrogenation products **10**, **11** and **12** through hydrogenation of aromatic rings of dibenzofuran at high H_2 pressure over Ni/Pt catalysts, followed by the cleavage of C-O bonds to produce **8**, **9** (pathways I and II). Moreover, **12** can also be converted to **6** and **7** through direct hydrogenolysis, and then, phenol was rapidly hydrogenated to cyclohexanol. Subsequently, the intermolecular dehydration reaction of **5** and **7** will happen to form O-free **4-1**. Due to the rapid hydrogenation dehydration rate, **6**, **7** were not easily detected during dibenzofuran conversion. It has been reported another pathway of HDO of DBF like III [8, 9, 11], however in this research there were little biphenyl or 2-hydroxyl biphenyl detected. So we proposed pathways I and II were the main reaction pathways in this research.



Scheme 1. Proposed Reaction Pathways of Dibenzofuran Conversion over Ni/Pt Catalysts.

4. Conclusions

In summary, bimetallic $Ni_{86}Pt_{14}$ catalyst exhibits good activity in the hydrodeoxygenation of dibenzofuran, at 200 °C and 1200 kPa H_2 pressure. Based on the TEM and XPS characterization, Ni/Pt bimetallic catalysts have smaller particle size than corresponding single metal catalysts and Ni were enriched in the catalysts surface. The combination of the two single component exhibits prominent effects overcoming the limitations of a single component catalyst. It is interesting to see that Ni/Pt catalysts were effective in the hydrogenolysis deoxygenation of sp2 C-O bond here. The structural characteristics of the Ni/Pt bimetallic catalysts may be the reason of their high catalytic activity and selectivity. We proposed hydrogenation of the aromatic rings is the first step, following by the C–O ether bonds cleavage and the deoxygenation of cyclohexanol to produce O-free cyclohexylbenzene. In addition, the aqueous phase reaction has the advantages of low cost, non-toxic and harmless to the environment and easy to separate organic products from the reaction system, which makes catalysts recyclable.

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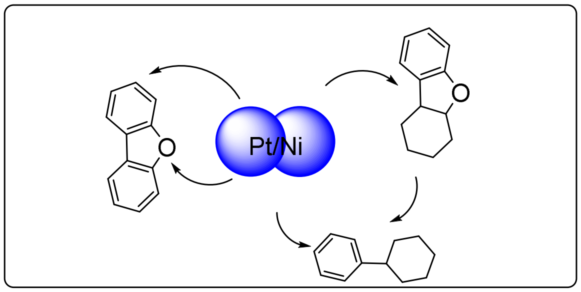

Hydrodeoxygenation of Dibenzofuran by Ni/Pt bimetallic Catalyst was achieved 99% of total conversion and 88% of selectivity of cyclohexylbenzene.